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Using a tight-binding Hamiltonian we study the Peierls distorted form of polyaniline, the pernigraniline base (PNB) polymer. Both bond order and ring torsional degrees of freedom are considered in the conformational relaxation. The geometrical and electronic structures of the localized solitonic and polaronic excitations are calculated. Comparison with available optical and magnetic measurements is made. Particular emphasis is placed on the spectroscopic and magnetic features of neutral solitons.

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Optical and Magnetic Signatures of Localized Excitations in

Pernigraniline: Role of Neutral Solitons

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Polyaniline is an interesting material due to its unusual transport, magnetic, optical and environmental properties [1]. In contrast to the simplest prototype conjugated polymer-polyacetylene, polyaniline offers a rich variety of distinct states accessible through protonation and oxidation/reduction. Despite much experimental work, our understanding of the system does not match that of polyacetylene. The simultaneous presence of the heteroatoms (the nitrogens) and the phenyl rings makes the theoretical modelling much less straightforward than that for polyacetylene. In this letter we show that it is nonetheless possible to understand much of the optical and magnetic properties from an SSH(Su-Schrieffer-Heeger) type Hamiltonian [2]. This allows a direct identification of the ground state as well as excited state lattice configurations of various forms of polyaniline.

In the following we present our results for pernigraniline base (PNB) polymer, Fig.1, the form of polyaniline with a Peierls gap in a degenerate ground state analogous to that of trans-polyacetylene. Our calculation reveals stable charged solitons and charged polarons as proposed earliear [3] as well as a new feature–stable neutral solitons. These neutral and charged solitons have energy levels displaced from midgap due to absence of charge conjugation symmetry. The charge and spin distributions as well as bond orders and ring torsional angles of these excitations are presented. The results are in good accord with available data.

Ignoring the ring rotation for a moment, we can write down the following SSH-like Hamiltonian

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hopping integral of the relaxed bonds. A bare value of $t_0 = 1.6eV$ leads to an average renormalized hopping integral of around $2.7eV$.

Following the above prescription one finds indeed two degenerate ground states for pernigraniline. They essentially confirm the correctness of the simple chemical notion of benzenoid ring and quinoid ring alternation. Based on this ground state degeneracy, solitonic excitations are expected. As discussed by dos Santos and Brédas [3] , these excitations resemble the irrationally charged solitons in A-B polymers [6] , but quantitative differences exist between the two models. In addition to the charged solitonic and polaronic states previously discussed by dos Santos and Brédas [3] , we have also studied the relaxed configuration of an electron-hole pair initially photo-generated in a neutral pernigraniline sample. It corresponds to two well-separated kinks. The effective charge e* of each kink is practically zero. The two gap states associated with the kinks are almost degenerate . Each of them is singly occupied. One can prove that in the adiabatic approximation those neutral spin solitons can be directly photogenerated in contrast to polyacetylene wherein only charged solitons are directly photogenerated [7] . This difference in the relaxation path is a consequence of the charge conjugation symmetry [8] being present in polyacetylene, but absent in PNB.

The energy gap thus calculated for PNB turns out to be about $1eV$, too small to account for the observed $2.4eV$ energy gap [9] . Hence we must examine the contribution of the ring rotational degree of freedom [5, 10].

We first discuss the ground state of pernigraniline. As before, there are two degenerate ground states. Each one has a distinct ring rotation dimerization pattern with a uniquely determined bond alternation pattern , i.e. the phases of the bond length and ring torsion order parameters are coupled. The ring that rotates further (53°) from the C-N-C plane is always benzenoid-like, while the quinoid-like ring twists a little (12°) from the C-N-C plane. This confirms the chemical intuition that it is harder to rotate double bonds than single bonds. For each ground state the energy gap is about 2.4 eV, more than double the gap calculated for bond only distortion; it is approximately the experimental value. This implies that the ring rotation dimerization contributes as much to the energy gap as the bond alternation does, consistent with a recent finding by Brédas et al. [12].

Each of the two dimerized ground states has identical electronic structure, the details of which can be directly probed by optical absorption experiment . For a given transition, the absorbance is proportional to the square of the dipole matrix element multiplied by the photon energy. The optical absorbance calculated for the ground state of PNB is displayed as the solid line in Figure 2(a). This calculation as well as other calculations to be described later have been done on a 112-site chain (16 C_6N units) with free boundary conditions. A Gaussian broadening of $0.2eV$ has been used to smooth the absorption curves. Compared to experiment [9] , the gap region between 3 and $6eV$ is too wide , the absorption in the low energy region (2 to 4 eV) is somewhat too large relative to the absorbance above 5 eV. Despite

is the bond order $(t_0 - \alpha\delta r_{ij})$. It is clear that the kink is essentially confined to two adjacent benzenoid-like rings. The chemical structure of the antisoliton $\overline{S}^0$ is the mirror image of S^0. Thus both neutral solitons have identical electronic structures. (It is noted that neutral solitons that are centered on two adjacent quinoid-like rings are unstable and decay into the benzenoid type soliton described here.) That explains why only one type of spin density distribution has been detected in neutral PNB samples [15, 16] . The wave function of the gap state is presented in Fig. 3(b). The probability of finding an unpaired spin at the single central nitrogen site is about 0.45, which is comparable to the value 0.6 deduced from the ESR measurement by Cromack et al. [15] and Long et. al.[16]. The average probability of finding the unpaired spin on each of the two adjacent benzenoid rings is about 0.1, which is also close to the experimental value.

In a pure electron-phonon model, we find that there is a short range repulsive interaction between two neutral solitons. With more neutral solitons generated at higher laser intensity, they start to overlap. Due to virtual hopping of the spins and the Coulomb repulsion between the two spins occupying the same gap state, the spins of two adjacent solitons will experience a Heisenberg antiferromagnetic exchange interaction. This weakly attractive potential will lock the spins into singlet pairs at low temperature. At high temperature the spins can be excited into triplet states. This picture qualitatively accounts for the temperature and laser intensity dependence of photoinduced susceptibilities [15, 16].

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ation energy of the charged pair by $0.5eV$ or more. Therefore the relative stability of charged versus neutral solitons awaits more accurate calculations.

The last type of elementary excitations are the polarons. Their spectroscopic features are depicted in Fig. 2(c). Among the three subgap absorption peaks, the lowest and the highest energy peaks are due to the hole polaron P^+, which is less strongly bound than the electron polaron P^-. The middle subgap absorption peak is due to P^-. The chemical structure and the wave function of the upper gap state of P^- are shown in Fig.4. It is clear that the net charge of the electron polaron is mostly deposited on the central ring (which is quinoid-like originally) and its two adjacent nitrogens. The ring torsional pattern near a hole polaron ...12^0, -50^0, 15^0, -41^0, 15^0, -50^0, 12^0....is more extended. It is centered about an originally benzenoid-like ring and reminiscent of the P^+ in leucoemeraldine base.[5] A hole polaron is more delocalized than an electron polaron because the valence band is wider than the conduction band.

Compared to the soliton pairs, the creation energy $1.9eV$ of an oppositely charged polaron pair is quite high. A polaron pair will therefore decay into a soliton pair unless the polarons happen to be located on different chains or both of them are pinned by some mechanism. As regards to the spectroscopic features shown in Fig. 2(c), they will be Coulomb shifted too [17] , but not as much as for solitons.

Experimentally Leng et al. [13] and Coplin et al. [14] have recently examined the long time component of the photoinduced absorption in more details and have

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# References

[1] A. J. Epstein and A. G. MacDiarmid, Makromol. Chem., Makromol. Symp. **51**, 217(1991).

[2] W.P. Su ,J.R. Schrieffer, and A.J. Heeger, Phys. Rev. B **22**, 2099(1980).

[3] M.C. dos Santos and J.L. Brédas, Phys. Rev. Lett. **62**, 2499(1989); ibid. **64**, 1185(1990).

[4] J. Yu, H. Matsuoka, and W.P. Su, Phys. Rev. B **37**, 10367(1988).

[5] J.M. Ginder and A.J. Epstein, Phys. Rev. B **41**, 10674(1990).

[6] M.J. Rice and E.J. Mele, Phys. Rev. Lett. **49**, 1455(1982).

[7] R. Ball, W.P. Su, and J.R. Schrieffer, J. Phys. (Paris) C **3**, 429(1983).

[17] D. Baeriswyl, D. K. Campbell, and S. Mazumdar, "An Overview of the Theory of π-Conjugated Polymers", in *Conducting Polymers*, edited by H. Kiess, Springer Topics in Current Physics (Springer, 1992).

[18] R. McKenzie and J. W. Wilkins, to be published.

[19] R.P. McCall, J.M. Ginder, J.M. Leng, H.J. Ye, S.K. Manohar, J.G. Masters, G.E. Asturias, A.G. MacDiarmid, and A.J. Epstein, Phys. Rev. **B 41**, 5202(1990).
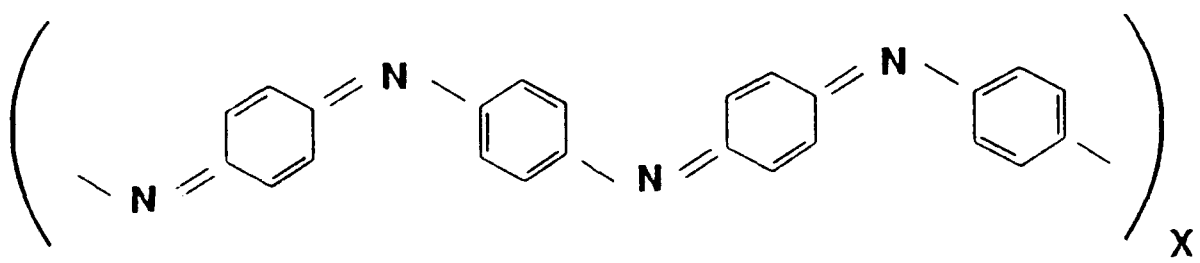
(b) Pernigraniline:
Charged Soliton Pair
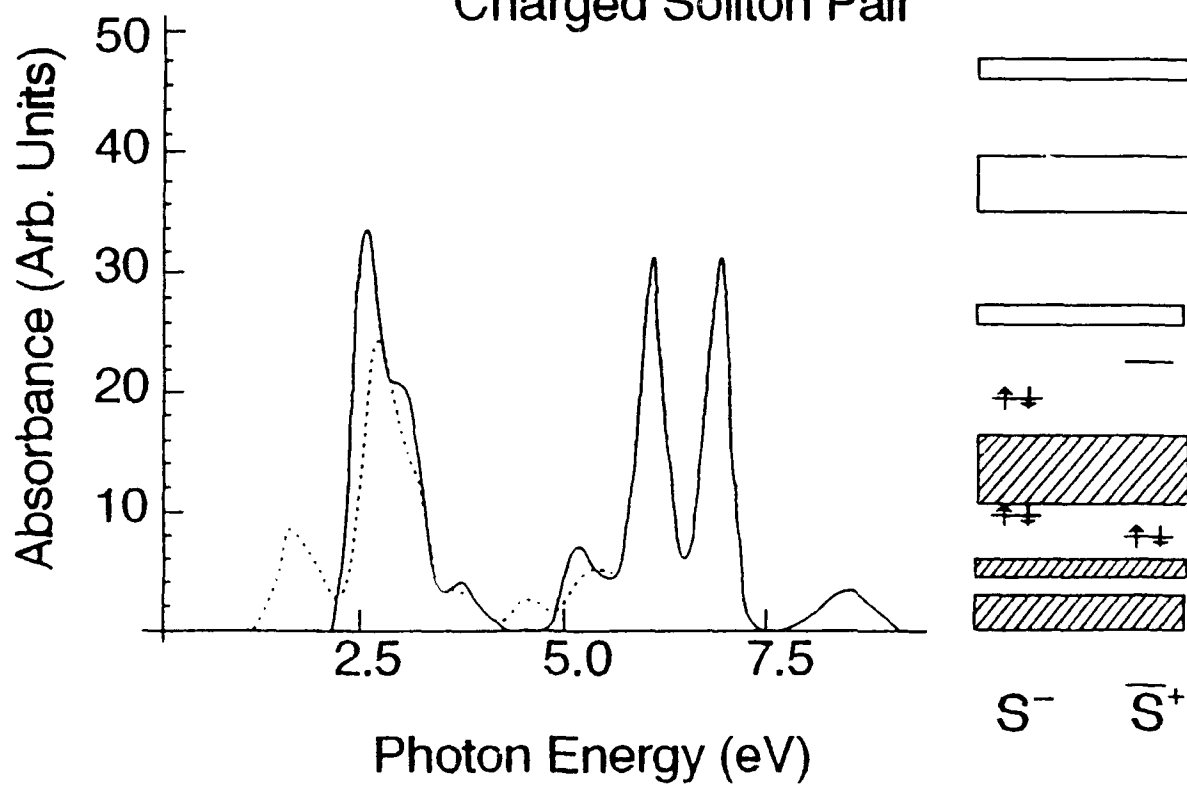
(a) Neutral Soliton: Bond Orders and Torsion Angles
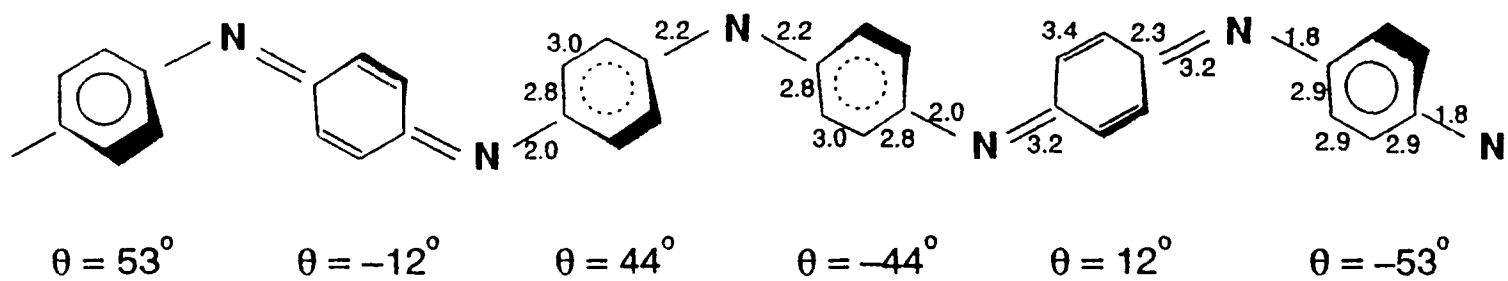
Electron Polaron: Gap State Wave Function

$$\theta = -52^{o} \qquad \theta = 35^{o} \qquad \theta = -52^{o}$$